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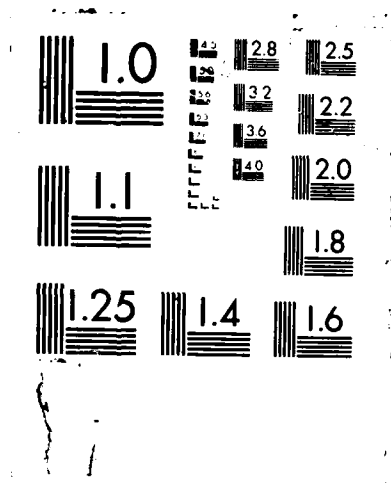   AFOSR-TR-88-0132 F49620-85-C-0065

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Results have been obtained by Fourier Transform Infrared Emission Spectrometry (FTIES) to determine the internal energy distribution in molecules whose states are consequent to three kinds of inelastic and/or reactive collision processes. (1) Free Jet Expansion. Gas that is vibrationally excited in the source by heating, corona discharge or chemical reaction is interrogated by FTIES after free jet expansion into vacuum. The observed marked departures from equilibrium give insight on RR, RT, RV and VV exchanges where R, T and V refer to rotatio al, vibrational and translational energy. Strong population inversions have been observed that may give rise to new laser systems. From experiments in which hot source gas was produced by comstion of fuel and oxidizer there emerged a "microjet burner" that seems a novel and useful tool for studying combustion processes. (2) Inelastic Scattering from Surfaces. When free jets of CO, CO_2, N_2O, and OCS are incident on a hot Pt surface the reflected molecul have enough vibrational excitation to be analyzed by FTIES. Vibrational and Rotational accommodation coefficients have been determined for these species over a range of surface [con]

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temperatures. (3) Reactive Scattering from Surfaces. FTIES analysis has been carried out on nascent CO_2 molecules formed by the catalytic oxidation of CO molecules incident on a Pt surface bathed in oxygen. Results indicated vibrational and rotational temperatures much higher than surface temperatures.

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carbon monoxide

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Molecular Collision Processes in Gases and at Surfaces

AFOSR Contract F49620-85-C-0065, Yale University

J.B. Fenn, Principal Investigator

Final Report
3/1/85-7/1/87

I. Introduction-Objectives

This report covers results obtained from experiments in our laboratory over the past three years. Our objective has been to understand the details of energy exchange during encounters between polyatomic molecules in the gas phase and between such molecules and surfaces. In particular, we have been interested in the distribution of rotational and vibrational energy consequent to inelastic and reactive collisions. Information on these distributions is obtained by infrared radiometry and Fourier Transform Infrared Spectrometry (FTIS). The collisions that we study occur: (a) during expansion of supersonic free jets in vacuo; (b) when two such jets intersect each other as uncollimated molecular beams; (c) when one such jet is incident upon a surface. Recently, have developed means of producing free jets of species that are electronically excited. Preliminary, results indicate that such jets may become useful sources of intense VUV raidation.

II. Achievements and Results

It will be convenient to consider separately each of three categories of experiments : (1) Those in which we look at the terminal states of species that have passed through a free jet expansion and reached the collisionless flow regime so that no further changes in state (due to collision) can occur; (2) Those in which two free jets intersect in the collisionless regime so that we can study the consequences of single gas-gas collisions over a range of translational and internal energy states; (3) Those in which the free jet flux is intercepted in the collisionless flow regime by a surface so that we can investigate inelastic and reactive encounters between molecules and surfaces. Results in each of these categories will be summarized briefly in what follows.

(1) <u>Terminal States in Free Jet Expansions of Heated Source Gas.</u> Over the years we have learned enough about free jet dynamics to relate the terminal states of free jet molecules to the source conditions and the relaxation rates for the various degrees of freedom that are active in the sense that they contribute to the enthalpy that is transformed into streaming translational kinetic energy during the adiabatic free jet expansion. Thus, in the parlance of gas dynamics, we are here concerned with heat capacity lags. In the very early days of free jet research the only kind of terminal state measurements we

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could carry out were on translational energy by velocity or time-of-flight (TOF) analysis of a molecular beam sample from the jet. Thus, the original objective of our spectrometric studies of free jet terminal states was to characterize the internal energies of molecules and thus to obtain information on the rates at which rotational and vibrational energy relaxed into translational energy. As is often the case in research, however, the experiments yielded some unexpected facets of the free jet expansion process that have offered rewarding opportunities for exploration. We will discuss results obtained with three different methods of exciting the source gas before expansion: (a) Simple heating; (b) Corona discharge; and (c) Chemical reaction (combustion).

(1a) <u>Simple Heating of the Source Gas</u>. We soon found that the terminal distributions of rotational energy in CO_2 were markedly non-Boltzmann but that they could be described extremely well in terms of a linear combination of two Boltzmann distributions. That is to say the jet gas was equivalent to a mixture comprising two populations, each at a different rotational temperature. This two-temperature model led to a consideration of the entropy that would be produced if there occurred a rotationally adiabatic relaxation that led to a single Boltzmann distribution at a rotational temperature intermediate between the values for each population. This rotational entropy deficit in the initial distribution is a sort of integrated surprisal and turns out to be a convenient measure of the departure from Boltzmannality. By means of FTIS measurements in the emission mode we had looked at the dependence of this entropy deficit on source pressure and temperature and concluded that its magnitude might be explained in terms of a competition between Rotation-Translation (RT) transfers that are "de-Boltzmannizing" and Rotation-Rotation (RR) transfers that are Boltzmanning. The competition is such that departure from Boltzmannality increases as the temperature of rotational freezing decreases. (1) We then extended the measurements to CO and mixtures of CO and CO_2 with He and Ar. In addition, we were able to use FTIS in the absorption mode to determine rotational distributions at the lower terminal "temperatures" that could be reached because the source gas did not have to be heated to 600 K or more to obtain emission from the jet molecules. (Stretching vibrations in CO and CO_2 do not relax during free jet expansion so that emission spectra can be obtained for jets from hot source gas.) These absorption results substantially confirmed our arguments about the RR-RT competition and together with the emission data comprise one of the few bits of experimental information that reveal the effects of RR transfers in bulk relaxation of rotational energy. (2)

Most recently we have examined the terminal states in free jets of OCS expanded from a heated nozzle. Although we have not yet completely analyzed the spectra a couple of interesting features have emerged. Both the vibrational and rotational energy distributions are non Boltzmann. Moreover, the forced-fit "temperature" of the bending mode is substantially higher than for the C-O stretch and thus probably higher than the source temperature if we can reasonably assume that T_{C-O} is about equivalent to T_o. It is noteworthy that V = 4 for the bending mode is nearly resonant with V = 1 for the C-O stretch. Thus we may be seeing the results of vibrational pumping process that takes place during the expansion.

(1b) <u>Corona Discharge in the Source Gas</u>. Although reasonably good absorp-

tion spectra can be obtained with a single pass of radiation through the jet, long averaging times as well as relatively high partial pressures of CO_2 or CO in the source gas are required. We have made several attempts to increase sensitivity using multipass optics without much success in part because of the limited brightness of broadband sources. FTIS in the emission mode is more sensitive if the source temperatures are high enough to excite an appreciable amount of vibration but with thermal excitation of vibration in the source gas there is always a price to be paid in the form of correspondingly high translational and rotational temperatures in the terminal state. Many years ago it had been shown in our laboratory that stable corona discharges could be maintained in source gas at pressures approaching 1000 torr and that such coronas could produce excited atoms and molecules. (3) Unfortunately, we did not then have any spectrometers that would allow us to examine the spectra of radiating species from discharge-excited jet molecules. Because in the work we have been describing we wanted to examine terminal distributions at the very low temperatures that can be reached only with relatively low concentrations of CO or CO_2 in a monatomic carrier gas (He or Ar) and at low source temperatures, we decided to try a corona discharge in the source gas to obtain vibrational excitation without raising the translational temperature appreciably. Rotational temperatures should also be lower, initially and finally, because they track translational temperature fairly closely.

The results were literally and figuratively exciting and seem to open up a host of opportunities for interesting research. In the case of CO, for which we obtained only small fraction excited to V=2 with source heating, we found substantial excitation up to the sixth level in the terminal gas with rotational temperatures as low as 10 K. Thus we have molecules in many vibrational states whose rotational relaxation we can follow and we may even be able to identify and characterize some VV transfers. Such transfers at the low translational (and rotational) temperatures that are readily obtainable in free jets have been shown capable of causing the kinds of vibrational population inversions found in the CO laser, for example. (4)

Even more interesting is the case of CO_2. Figure 1 shows a spectrum that we find particularly intriguing. In the first place the rotational distribution is much narrower than we ever achieved with excitation by heating. The combination bands are now out from under the shadow of the P branch of the fundamental, so we will be able to ascertain the extent of relaxation of the bending mode that we think we had seen in earlier experiments but were unable to resolve and follow because of the overlap of the fundamental rotational lines. More interesting is the appearance of a new band about 70 cm^{-1} to the red of the fundamental. Its intensity is about 15 per cent of the fundamental band but it never showed up at all in spectra obtained with thermal excitation of vibration. There seems to be little doubt that this new band is due to the isotope $^{13}CO_2$. The question is: why does it appear? We do not believe that the natural abundance of ^{13}C is 15 per cent instead of 1 per cent. Nor do we think that we have somehow achieved a great concentration of the isotope in a simple expansion. We suspect that something like the following scenario takes place: a vibrationally excited $^{12}CO_2$ encounters a $^{13}CO_2$ and transfers a quantum of vibrational energy. The excess 70 cm^{-1} of energy goes into rotation of the two partners, probably splitting evenly between them. Because the rotational

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temperature is so low there are very few ground state (vibrational) $^{12}CO_2$ molecules with high enough J levels to serve as partners for the reverse reaction, and/or the excited $^{13}CO_2$ is rotationally cooled before it can undergo the reverse reaction. The net result is that the $^{13}CO_2$ is vibrationally pumped in a preferential way. Similar pumping of heavier isotopes by V-V transfers has been observed in diatomic molecules (CO and NO) but not in the clean and clear cut way that this free jet experiment seems to exhibit. (5) To us these results fairly cry out for further investigation.

In another variation on the corona-discharge excitation theme we have been investigating free jets as sources of UV radiation. The so-called "Hopfield Continuum", which extends from about 600 Å to 900 Å, has long been a spectral regime of great interest for VUV spectroscopy. The widely used source of photons in this wavelength range has been the excited helium dimer or "excimer" often produced by CW electrical discharges [Radiofrequency (RF), Microwave (MW) or Direct Current (DC)] in helium gas passing through a tube a centimeter or less in diameter and several tens of centimeters in length. (It is to be remembered that the attractive force between two ground state He atoms is too small to allow a stable bound state except perhaps at temperatures near absolute zero. On the other hand the attractive force between an excited and a ground state He is substantial.) Because there are no materials available that are effective as windows for radiation at these wavelengths, the end of the tube must be open to let the photons out into the chamber containing the monochromator or other device that makes use of them. This chamber must be evacuated because the radiation is strongly absorbed by all gases except monatomic helium. In order to keep the pumping speed requirements at a reasonable level one would like to maintain the gas in the tube at pressures as low as possible without sacrificing too much radiation intensity. Moreover, it is difficult or impossible to maintain a stable RF or Microwave discharge at high pressures. Therefore, usual operating pressures are less than a few torr. Typically, many watts of power are dissipated in the gas so that there must be substantial provision for cooling in order to keep the gas temperature from rising too high. The combination of relatively high gas temperature and relatively low gas pressure means that the dimer concentration is low. Fortunately, helium monomer does not absorb in the Hopfield continuum and photons striking the tube walls at grazing incidence are reflected. Consequently, by using long tubes one can achieve total dimer populations sufficient to provide photon fluxes at useful levels, even though the gas density is low. The efficiencies of many of these devices are abysmally small.

The preceding remarks relate to the characteristics of CW VUV sources. There have been recently developed some intermittent or pulsed devices that overcome some of these problems but they have not yet been very effective in producing excimers of helium and so cannot provide photons at wavelengths below 1000 Å. They have been highly developed for producing rare gas halide excimer "lasers" that can produce intense UV radiation at longer wavelengths for short periods, e.g. microseconds or less per pulse, and are commercially available.

It follows from fairly elementary thermodynamics that the way to produce high dimer concentrations is to combine high pressures with low temperatures, in diametric opposition to the conventional practice we have just outlined. As

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pointed out earlier, free jets can easily achieve the combinations of temperature and density that lead to cluster formation. Very recently, we have carried out a few simple experiments that take advantage of these properties of supersonic free jets and confirm this principle that has been understood since Le Chatelier and undeniable since Gibbs. The results seem to reveal promising possibilities for VUV sources of remarkable intensity and simplicity.

As already mentioned, some 15 years ago in our laboratory J. Q. Searcy found that it was easy to strike and maintain a DC corona discharge in the source chamber for a helium free jet. Moreover, he found that a beam extracted from such a jet contained useful concentrations of metastable He atoms. (3) He also noted a substantial flux of photons which gave rise to a signal from his electron multiplier detector much larger than the signal from metastables. He was able to discriminate between these two sources of signal by means of a simple rotating shutter that introduced a time delay between the signals from photons and from metastable atoms because of the great difference in their velocities.

In light of these results the thermodynamic arguments set forth a few paragraphs ago persuaded us years ago that we ought to try experiments that we finally got around to carrying out just recently. We provided a simple glass nozzle with liquid nitrogen cooling and struck a DC corona discharge in helium source gas. As a detector we used an available Channeltron multiplier whose response to photons has a fairly broad maximum in the range between 500 $\mathring{A}$ and 1000 $\mathring{A}$. These components were mounted in one of our large vacuum chambers equipped with a baffled 32-inch diffusion pump that provides an effective pumping speed of about 15,000 liters/s. With nozzle diameters of .05 mm we can operate with source pressures in the Kilotorr range. We quickly found that even when it was located at a radial distance of 30 cm from the jet axis, where the photon intensity should probably be lowest if the distribution is not isotropic, the detector saturated until we stopped it down with an aperture only 0.1 mm in diameter. Assuming an isotropic distribution and the manufacturers specifications for quantum efficiency we concluded that the total photon flux (assuming an isotopic distribution) corresponded to about 0.4 watts. The electrical power input was only 1.0 watt! Moreover, the nozzle diameter was only 0.04 mm. Therefore, the photon flux intensity based on the nozzle diameter was of order 30 kw/cm^2. We have further found that the photon intensity in the axial direction is much higher than in the radial direction but we have not yet separated out in a quantitative way the contribution due to metastables. (Ions were removed with a grid at suitable voltage.) We infer from the Searcy experiments that most of the signal is due to photons.

Because we had no means of determining the spectral distribution of the emitted radiation we could not determine whether it was due simply to resonance radiation from excited monomer. We were inclined to believe until recently that it was due to excimers because the intensity increased exponentially with source gas density. A linear dependence would be expected for resonance radiation from the monomer. It seemed for a while that our optimistic inferences were without substance. When Wolfgang Groeger, who had performed these experiments in our laboratory returned to Germany. He gained access to a VUV monochromator at the Max Planck Institute in Goettingen and found in some preliminary experiments

with a similar source no evidence of excimer radiation. While this finding was disappointing we did not give up hope. Then, more recently Professor R.O. Watts and his colleagues, acting on our suggestion also carried some similar experiments. They found that by placing the discharge electrodes right at the nozzle exit, they did indeed get excimer radiation with both argon and helium (6) Thus, thermodynamics has been indicated and the way seems open for some very rewarding and exciting research.

(1c) <u>Chemical Reaction (Combustion) in the Source Gas.</u> Very recently in our laboratory we have taken advantage of the ability of hot surfaces to stabilize combustion in the absence of flame holders. By heating the walls we have been able to stabilize a combustion zone under choked exit flow conditions in small bore alumina tubes (1.5 to 3.0 mm or more in diameter). The exit inside diameter is reduced to say 0.2 mm to form a sonic nozzle through which the combustion products emerge into vacuum in a supersonic free jet. Emission spectra of the exhaust products after they have expanded to the collisionless regime of free molecule flow are shown in Fig 2. Important and intriguing features of these spectra are the fact that the rotational temperatures obtained from Boltzmann plots are much lower than the temperature in the combustion zone so that the spectra are much cleaner than can be obtained without the rotational cooling due to the free jet expansion. The vibrational temperature is mostly unchanged during the expansion because relaxation rates for vibration are orders of magnitude slower than for rotation. Indeed, from the lowermost spectrum in Fig. 2, in which the CO spectrum is dominant because the mixture was fuel-rich, it is possible to infer a vibrational temperature of about 1370 K from the relative intensities of the $V = 2$ and the $V = 1$ transitions. The CO rotational temperature from the same spectrum is 355 K. Interestingly enough, the rotational temperature for CO_2 in the same jet was only 200 K. The difference invites the conclusion that the CO rotational temperature might have been higher before the expansion and suggests that maybe we are sampling and "freezing" the composition of species from intermediate stages in the combustion process, or it may be that CO_2 has a faster rotational relaxation rate in the free jet. The average residence time in this particular burner is between about 0.5 and 1.0 ms, less than a μs of which is required for freezing composition in the expansion. In light of this result it would be interesting to look at the terminal states in the expansion of source gas which is a mixture and is excited by simple heating or by a corona discharge. We should be able to learn something about RR exchange between different kinds of molecules.

Because the combustion gases are in vacuo after they have passed through the free jet it also becomes straightforward to analyze them with a mass spectrometer. Figure 3 shows a schematic diagram of the burner along with two representative mass spectra taken with an available quadrupole that is 20 yrs old and so tired that it worked reasonably well only about one or two hours a week. Moreover, its effective mass range was only up to about 150 daltons. Consequently, we could not in these preliminary experiments search very effectively for soot precursors in any attempt to trace the sequence of intermediates in soot formation. We did identify acetylene, diacetylene and a peak at 73 daltons in a fuel rich flame that would correspond to the very strange C_6H radical. It is noteworthy that the entrance to the ionizer for the spectrometer was about 1000 nozzle diameter downstream from the burner nozzle so that the

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signal was several powers of ten smaller than could be readily achieved by decreasing the distance between nozzle exit and ionizer. Even at these large distances the signal/noise ratio was very high so with a good spectrometer it would be very easy to detect and identify trace species at extremely low concentrations in the exhaust gas.

We have also done a few experiments in which two parallel plates were disposed on either side of the jet axis in series with a dc power supply and a sensitive ammeter. We found currents up to tens of nanoamps with emf differences between the plates of a few tens of volts. Under fuel rich conditions there were substantial deposits of soot on the two plates with distributions that seem to indicated clearly that the soot particles must have been charged. Moreover, the character of the deposits was very different on the two plates, indicating a difference in the nature of the particles depending upon whether they were negatively or positively charged. In another configuration we detected ions by admitting them through a very small aperture to a channeltron multiplier. From the location and size of the aperture and the size of the signal we estimated that the total flux of ions in the jet was about a microamp, consistent with the results of the conduction experiment. In other words there are lots of ions in the jet exhaust and it would not be difficult to analyze them with a mass spectrometer and obtain information on ion formation processes in this "world's smallest jet engine".

It seems clear to us that this new microjet burner offers exciting possibilities for research on chemical kinetics of combustion reactions including formation of soot and ions. It avoids many of the problems and limitations that plague similar studies in flames. Most flame probing must be done at low pressures in order to achieve any kind of spatial (time) resolution and one has always to worry about perturbation of the flame structure, temperature or gas composition when samples are withdrawn from such flames by means of probes. No such pressure limitation occurs in the microjet burner. Wall or surface perturbations are minimized because the gas we interrogate can always be taken from the core or axis of the jet which we know from previous work does not "see" the nozzle walls. The extremely rapid drop in temperature and density in the free jet expansion should effectively freeze composition and vibrational energy states in a much shorter time than can be realized in sampling tube. The low rotational temperatures brought about by the expansion greatly improves the resolution of vibrational and electronic energy levels that can be obtained with photon spectroscopy. The direct transport of species from the combustion zone into vacuum greatly facilitates and enhances mass spectrometric analysis of both neutral and ion species. Further, we would note that as is also the case in the much more complex and awkward well-stirred reactor developed by Longwell and his colleagues, the nature of the combustion process in the microjet burner is much more akin to what goes on in a real jet engine than is combustion in laminar premixed or diffusion flames. (7) Finally we observe that in many ways the "exhaust plume" from our microjet can mimic the exhaust plumes of jet engines flying at very high altitudes. Consequently by means of mass analysis of ions and neutrals as well as by photon spectrometry over the entire wave length range from the vacuum ultraviolet to the far infrared we can hope to elucidate relationships between combustion chamber conditions and plume characteristics for real propulsion systems. Note that because the microjet exhausts into vacuum we

are not limited to those portions of the spectrum for which the atmosphere is transparent. Equivalent measurements in the case of most real engines or larger scale models thereof are much more difficult to make because they must be done in high altitude flight tests or in one of the relatively few large scale vacuum systems. Of course, we do not claim that the microjet burner will faithfully model large scale systems but judicious interpretation of the observations we can make should provide useful insights. A paper on the microjet burner has been submitted for publication.

(2) <u>Inelastic Gas-Gas Scattering.</u> Consequent to Air Force interest in the infrared radiation characteristics of rocket exhaust plumes our laboratory several years ago undertook some experiments aimed at determining the cross section for translational-vibrational (TV) excitation of CO molecules by collision with N_2, O_2, H_2 and Ar. Indeed, it was this research that started our continuing affair with infrared radiometry and a spectrometry. The approach was to oppose uncollimated beams (free jets in the free molecule flow regime) so that the intersection region was in the field of view of an infrared detector (InSb) whose maximum sensitivity is at the wavelength of photons from the asymmetric stretch mode of CO_2. We were finally able to obtain some reasonably reliable data but the signal-to-noise (S/N) problems were formidable. (8) The collision velocities of interest were 2 to 10 Km/s, a range that we invaded up to about 6 km/s by a combination of aerodynamic acceleration of both collision partners with He or H_2 (seeding) and increases in source temperature for the projectile molecules, N_2, O_2, Ar and H_2. In order to take advantage of frequency and phase discrimination we modulated the CO_2 (cold) jet with a motor driven rotating chopper in the usual way. It turned out that a major source of noise was the reflection of photons from the heated nozzle by the blades of the chopper. We tried all kinds of baffling and managed to achieve usable S/N ratios under some conditions. Attempts to extend the measurements to the TV excitation of H_2O molecules were not very fruitful because the cross sections and/or oscillator strengths for H_2O were enough smaller so that noise wiped out the signal.

An important prerequisite to success in this experiment is calibration of the detection system so that the signal can be related to the concentration of excited CO_2 molecules in the field view. We achieved this calibration by chopping the CO_2 beam when its source was hot, taking advantage of the absence of vibrational relaxation of the thermally excited CO_2 molecules during expansion. This calibration requirement meant that we could not modulate the CO_2 flow simply by passing it through a pulsed nozzle because of the need for source temperatures up to 900 K or so. Recently, we have found a way to modulate the flow of hot CO_2 with a pulsed nozzle that is not itself exposed to high temperature. Substantial gains in S/N have been achieved by this method that should be applicable not only in our TV excitation measurements but also in other experiments in which modulation of a hot source gas is necessary.

The essential features of the modulation system are simple. The modulated flow of cold gas from the pulsed nozzle is passed through a stainless steel tube (4.5 cm long with a bore of 0.5 mm) and intersects the free jet about 6 nozzle diameters downstream from the exit. If the pulsed flow is sufficiently large (source pressure sufficiently high) the heated jet is deflected enough so that

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none of its gas reaches the field of view of the detector. Figure 4 shows the detector signal dependence upon deflection gas (Ar) source pressure. For these conditions (CO_2, P_o = 900 torr) it seems clear that at Ar source pressure above 200 torr the signal is at the maximum value corresponding to nearly complete absence of any radiation contribution from of the hot CO_2 when the deflecting gas is flowing. Similar results have been obtained with N_2, O_2 and He as deflecting gases at frequencies from 75 to 350 Hz and with P_o for CO_2 from 50 to 1500 torr. Figure 5 shows the signal from CO_2 molecules at two different source pressures excited by TV collisions with N_2. The CO_2 flow was modulated by Ar as the deflection gas. We have extracted some preliminary values of excitation cross sections from these data and find them to be somewhat smaller than but reasonably consistent with our earlier results which had much more scatter.

We estimate that S/N values are at least three orders of magnitude higher with this gas dynamic deflection technique than with a rotating chopper under other wise similar conditions. For example, with mechanical chopping we were unable to obtain S/N as high as unity with H_2O at 1200 torr and 1100 K in the source. With gas dynamic deflection we obtained S/N of at least 10 with H_2O at only 100 torr and 700 K.

The disadvantage of this modulation technique is the increased gas load on the pumping system. In our experiments the additional load was reflected in an increase of background pressure from 4×10^{-5} to 5×10^{-5} torr so the net increase was only about 1×10^{-5} torr. We have not yet optimized the configuration and are persuaded that we can substantially decrease the flow requirement for deflection gas.

(3). <u>Inelastic and Reactive Scattering of Molecules by Surfaces</u>. It is to be remembered that in a free jet expansion from an axisymmetric nozzle the gas density decreases with the square of distance from the nozzle exit. In these experiments we intercept the jet flux with a target surface sufficiently far downstream so that the mean free path in the jet gas is of the same order or larger than the jet diameter and the lateral dimension of the target surface. Under these circumstances molecules incident on the surface are in their terminal state (determined by source conditions) and undergo no collisions with molecules reflected from the surface. Thus, any changes in state between incident and reflected molecules have been the result of single collisional encounters between the molecules and the surface. In effect, the jet flux is an uncollimated molecular beam whose divergence of streamlines means that effects due to angle of incidence cannot be resolved nearly as well as in a true collimated beam experiment. On the other hand, the total incident flux is sufficiently large to provide enough reflected molecules for spectral analysis by FTIS that is not feasible with a collimated beam. We will review briefly the results we have obtained with such jet surface experiments for both elastic and inelastic surface collisions.

(3a) <u>Inelastic Surface Scattering</u>. Our first experiments were with CO and CO_2 scattered from a polycrystalline platinum surface heated to temperatures as high as about 1500 K. For CO_2 about one in five incident molecules was excited to V = 1 in the asymmetric stretch mode and the rotational energy of these excited molecules had a Boltzmann distribution corresponding to temperature

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ranging from 0.4 to 0.6 of the surface temperature. For CO molecules, the probability of excitation was about 0.7. Moreover, unlike the case of CO_2 there were enough molecules excited to the V = 2 mode to allow us to deduce a vibrational temperature that was identical with the surface temperature. Also unlike the CO_2 case the rotational energy for CO had a non-Boltzmann distribution. In terms of average energy the rotational accommodation was roughly the same as for CO_2 ranging from 0.4 to 0.6 of what would be expected for equilibrium at the surface temperature. (9)

We also did some experiments with NO and found its behaviour similar to that for CO. Vibration seemed to be almost completely accommodated to the surface temperature but the rotational energy had a non-Boltzmann distribution with a total rotational energy of only about half that to be expected for equilibrium with the surface. It was also possible to distinguish between the $2\pi 3/2$ and the $2\pi 1/2$ electronic states and to arrive at a "spin orbit temperature" for the scattered molecules that showed a very interesting and strong dependence on the rotational level. Indeed, it reached to a value below room temperature at the lowest J levels even though the surface temperature was 1430 K. (10)

Most recently we have examined the behaviour of OCS during surface scattering. The rotational distribution is non-Boltzmann and corresponds to an energy accommodation of about 0.5 at surface temperatures from 500 K to 1200 K. We were able to determine temperatures for the bending and C-O stretching modes and found them to be respectively 1.0 and 0.45 of the surface temperature. A paper on these results has been submitted to the **Journal of Chemical Physics.**

(3b) <u>Reactive Surface Scattering.</u> Literally and figuratively more exciting were the experiments in which the jet flux to the platinum surface comprised a mixture of CO and O_2. Product CO_2 molecules were formed by surface catalyzed oxidation in sufficient abundance and with sufficient internal excitation to be analyzed by FTIS in the emission mode. We found that within each degree of rotational and vibrational freedom the distribution of energy levels was sufficient Boltzmann to be assigned a temperature. These temperatures were all higher than the surface temperature but were all different. From their values and an energy balance we were able to obtain what we think is a fairly complete accounting for the disposition of the activation energy contained in the transition state for the surface catalyzed reaction and to draw some inferences as to the configuration of that state. Although preliminary results were reported several years ago a detailed account of this study has just been published. (11,12)

A collaborative effort by Kori and Halpern in our laboratory determined the vibrational energy distribution in CO formed by the reaction of O or O_2 in a jet incident on a platinum surface having sub-monlayer coverages of C atoms. The product molecules had a near Boltzmann distribution of vibrational energy over levels up to V = 7. From a surprisal-like analysis they concluded that the transition state might well have been a complex comprising CO bonded to three surface Pt atoms. (13)

In another collaboration with professor Gary Haller's group we have been

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successful in obtaining time-resolved spectra of CO_2 molecules formed by surface catalyzed oxidation of CO on Pt. (14) We bathe the surface in a steady flux of O_2 and periodically flood it with a puff of CO from a pulsed nozzle. The FTIS software triggers the pulse and starts the interferometer scan after a specified time delay which is successively increased. The computer stores the digitized scans and subsequently reconstructs from them a composite inerferogram equivalent to one taken nearly instantaneously at a particular time after the puff arrives on the surface. Figure 6 shows a sequence of such spectra at 30 μ sec intervals. The key variable is surface coverage of oxygen which first goes down as the incident flux of CO is high and then is gradually restored by the steady flux of O_2. The advantage of this experiment is that it provides a wide range of surface coverage without an appreciable change in surface temperature. Although the spectra are at relatively low resolution we can obtain estimates of vibrational and rotational temperatures from the width of the distribution and the position (in cm^{-1}) of its centroid. We find that vibrational and rotational temperatures both decrease as surface coverage decreases, the former somewhat more slowly than the latter. (15) In the case of Pd surfaces there seems to be much less dependence of T_R and T_V on coverage. We remain in the throes of trying to understand and explain these observations. Clearly much remains to be done.

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Cumulative Publication List

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